

# Interstitial bismuth dimers and single atoms as possible centres of broadband near-IR luminescence in bismuth-doped glasses

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## Abstract

Absorption, luminescence and Raman spectra of interstitial bismuth atoms,  $\text{Bi}^0$ , and negatively charged dimers,  $\text{Bi}_2^-$ , in aluminosilicate, germanosilicate, phosphosilicate and phosphogermanate glasses networks are calculated by time-dependent density functional method. On grounds of this calculation an extension of our previously suggested model of broadband near-IR luminescence in bismuth-doped glasses is put forward.

*Key words:* Computer simulation; Glasses; Bismuth; Luminescence

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## Introduction

Near-IR broadband (1100 – 1400 nm) luminescence in bismuth-doped glasses discovered in Refs. [1, 2] is being studied intensively. By now the luminescence has been observed in many bismuth-doped glasses, such as aluminosilicate (e.g. [1–7]), aluminogermanate (e.g. [4, 8–10]), alumoborate (e.g. [10–12]), aluminophosphosilicate, aluminophosphate, aluminophosphoborate [4, 12–14], chalcogenide [15, 16] and in several bismuth-doped crystals ( $\text{RbPb}_2\text{Cl}_5$  [17], FAU-type zeolites [18],  $\text{BaB}_2\text{O}_4$  [19]). The bismuth-related IR luminescence is used successfully in laser amplification and generation (see, e.g. [20, 21]). The present

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state of research and applications of near-IR luminescence in bismuth-doped glasses are examined in the recent reviews, Ref. [22, 23].

However there is no commonly accepted model of the IR luminescence center. Several models are suggested, such as electronic transitions in  $\text{Bi}^+$  [11, 13–15],  $\text{Bi}^{2+}$  [15] and  $\text{Bi}^{5+}$  [2–4, 8] interstitial ions, in  $\text{BiO}$  interstitial molecules [6],  $\text{Bi}_2$ ,  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$  interstitial dimers [5, 9, 16, 24, 25], other bismuth clusters [9],  $\text{BiO}_4$  complexes with tetrahedral coordination of the central bismuth ion [26].

In our opinion there is good evidence for negative bismuth dimers being the luminescence centres (see e.g. [7, 16, 25]). However, up to now, there are no convincing explanation of changes in absorption and luminescence spectra with glass composition (see e.g. Refs. [21, 23]). In the context of the  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$  dimers as centres of the IR luminescence it would appear reasonable that such changes are caused by Stark shift and splitting together with certain rearrangement of dimer states in glass network electric field. The latter does obviously depend on glass composition.

Alternatively, there is an evidence that single Bi atoms and ions do occur as well in the bismuth-doped glass host. We studied Raman scattering of Ar laser 457.9 nm-light in optical fibres with bismuth-doped aluminosilicate glass core and observed a narrow intensive band in the low-frequency part of the Raman spectra, near  $110 \text{ cm}^{-1}$  (Ref. [25], Fig. 4, "a" band). Our calculation [25] of neutral single bismuth atom,  $\text{Bi}^0$ , and negative single bismuth ion,  $\text{Bi}^-$ , incorporated in aluminosilicate host in the sixfold ring interstitial sites proved both  $\text{Bi}^0$  and  $\text{Bi}^-$  have three vibrational modes practically not mixed with any vibrations of the rings. The frequency of these vibrational modes are found to fall in the  $75 - 105$  and  $85 - 130 \text{ cm}^{-1}$  ranges, for  $\text{Bi}^-$  and  $\text{Bi}^0$ , respectively (see Fig. 5 in Ref. [25]). One mode corresponds to displacement of the interstitial bismuth atom along the rings axis and the other two correspond to transverse displacement of the atom. All three vibrational modes are Raman active, scattering in the transverse vibrations being an order as intensive as in the longitudinal ones. Hence the Raman band near  $110 \text{ cm}^{-1}$  in bismuth-doped aluminosilicate glass may be indicative of single bismuth atoms,  $\text{Bi}^0$ , or negative ions,  $\text{Bi}^-$  in sixfold ring interstitial sites of the glass network. Recently electronic transitions in the  $\text{Bi}^0$  atom has been supposed to be responsible for the near-IR luminescence in bismuth-doped glasses [27].

The aim of this work were to verify the assumptions regarding both the network electric field and the interstitial bismuth atoms by immediate calculation of optical properties of interstitial Bi atoms and ions in networks of silica- and germania-based glasses.

## Calculations

In our previous works [24, 25] we used calculated data for free negatively charged  $\text{Bi}_2$  dimers to explain absorption and luminescence spectra of bismuth-doped glass. Experimental data available for free  $\text{Bi}^0$  atom were used to the same purposes in Ref. [27]. However an influence of glass network (interstitial electrostatic field, in essential) must be taken into account to discuss optical spectra of interstitial dimers and atoms.

We performed quantum-chemical calculation of interstitial electric field in network of glasses of several compositions (silica, germania, aluminosilicate, germanosilicate, phosphosilicate, phosphogermanate). Cluster approach was used to model the atomic environment of interstitial sites. Two coaxial sixfold rings each formed by  $\text{SiO}_4$ ,  $\text{GeO}_4$  (for germanosilicate glasses with low germania content),  $\text{AlO}_4$  or  $\text{O}=\text{PO}_3$  tetrahedra or  $\text{GeO}_6$  octahedra (for germanosilicate glasses with high germania content) were incorporated in proper numbers in the clusters. The distance between the ring centres was optimized during the calculations. To ensure aluminum atoms being fourfold coordinated, extra electrons were placed in the aluminum-containing clusters, one electron per aluminum atom. In  $\text{GeO}_6$ -containing clusters two extra electrons were added per sixfold coordinated germanium atom to make it be stable in this coordination. Dangling bonds of the outer oxygen atoms in the clusters were saturated with hydrogen atoms. All calculations were carried out with GAMESS (US) quantum-chemical code [28] by DFT method using BLYP functional which is known to provide nice agreement of calculated geometrical parameters with experimental data. We used the bases and effective core potentials developed in Ref. [29]. One  $d$ -type polarization function with  $\zeta = 0.8000$  a.u. was added in the basis for each oxygen atom. Standard 3-21G basis was used for hydrogen atoms.

Quantum-chemical modelling of configuration and vibrational properties of  $\text{Bi}_2$ ,  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$  dimers and of single  $\text{Bi}^0$  atom and  $\text{Bi}^-$  ion in aluminosilicate network was performed in our previous works [24,25] using the above-described cluster approach. Calculated configuration for  $\text{Bi}_2^-$  interstitial dimer was presented in figure 3 of Ref. [25] for aluminosilicate glass. In the present work such calculations were repeated for silica, germania, germanosilicate, phosphosilicate, and phosphogermanate clusters. The equilibrium configurations of negatively charged dimers, both  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$ , in the interstitial site formed by two sixfold rings are found to be quite similar in all these networks: the dimers are aligned along the common axis of the rings, the first bismuth atom being practically in the center of one ring and the second atom being between two rings. Again, equilibrium position of  $\text{Bi}^0$  atom and  $\text{Bi}^-$  ion are found to be between two six-rings in all these networks. As a representative example, calculated configuration of aluminosilicate glass cluster with  $\text{Bi}^0$  interstitial atom

is shown in figure 1. Such configurations turns out to be highly stable for both dimers and atom or ion: bismuth atoms do not form bond with any atom of the rings and returned to the equilibrium positions even after dimer or single atom is displaced considerably from that position. Vibrational properties of interstitial  $\text{Bi}^0$  atom and  $\text{Bi}_2^-$  dimer in all these networks are found to be quite similar to those calculated in Ref. [25] for aluminosilicate host (see above).

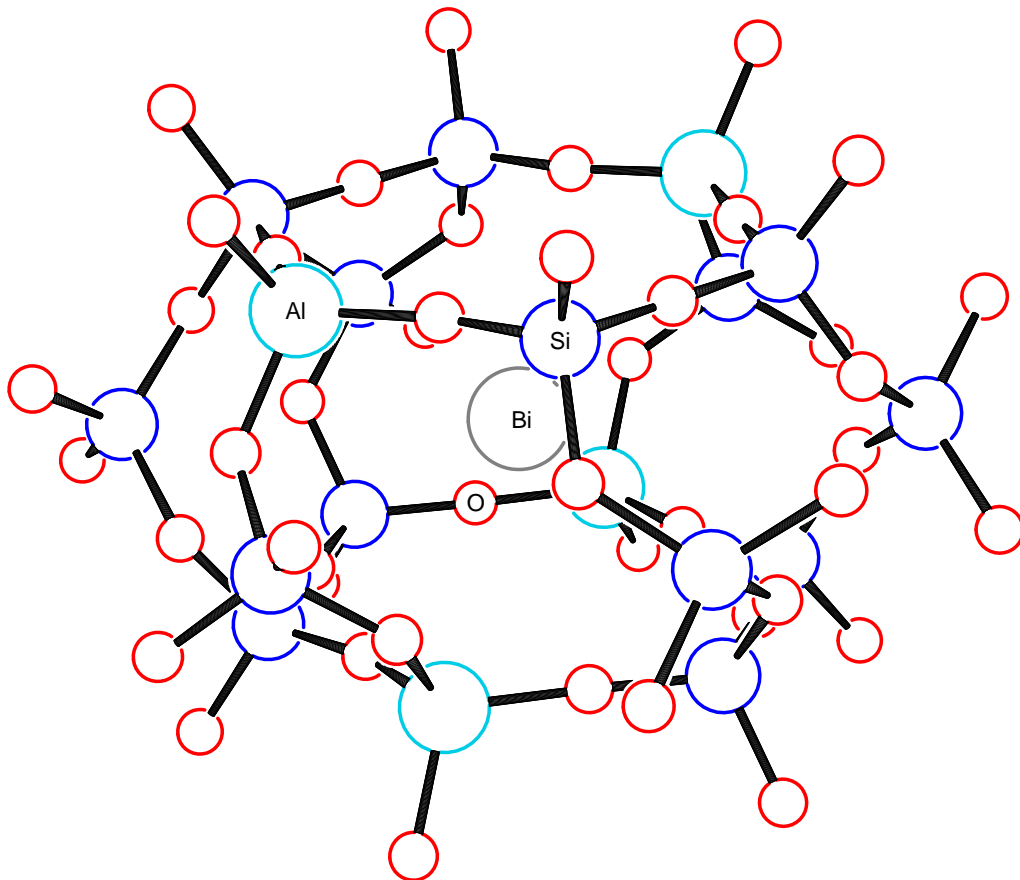


Figure 1. Calculated configuration of  $\text{Bi}^0$  atom in the sixfold-rings interstitial site of aluminosilicate glass

Electric field strength was calculated in the point of the  $\text{Bi}^0$  atom position (or, what is the same, near the bismuth atom of the  $\text{Bi}_2$  dimer which is situated between two sixfold rings) and in several (8 – 10) points in its vicinity. The value averaged over all such points was used in further calculations of optical spectra. The mean electric field strengths in ring interstitial sites calculated for several glass compositions are given in table 1. As evident from these data, the interstitial electric field is found to be approximately the same in silica, germanate and germanosilicate (with low germania content) hosts but considerably higher both in glasses containing aluminate or phosphate component and in germanosilicate glasses with high germania content. This is attributable

to charged ( $\text{AlO}_4$  and  $\text{GeO}_6$ ) or strongly dipole-polarized ( $\text{O}=\text{PO}_3$ ) structural units in the rings around interstitial bismuth sites in such glasses.

Table 1

Calculated electric field in sixfold ring interstitial sites of glass network

Ring composition	Electric field, 0.001 a.u.
$6\text{SiO}_4$	2
$6\text{GeO}_4$	2
$4\text{SiO}_4 - 2\text{GeO}_4$	2
$4\text{SiO}_4 - 2\text{AlO}_4$	5
$4\text{SiO}_4 - 2\text{GeO}_6$	7
$4\text{SiO}_4 - 2\text{O}=\text{PO}_3$	7
$4\text{GeO}_4 - 2\text{O}=\text{PO}_3$	10

Optical spectra calculations were performed by time-dependent density functional theory (TDDFT) method using Octopus program [30] and Hartwigsen-Goedecker-Hutter pseudopotentials [31] with spin polarization and spin-orbit interaction taken into account. PBE density functional [32] was used in the ground-state calculation. To obtain the linear optical absorption spectrum of the system, the Octopus code excites all frequencies of the system by giving certain (small enough) momentum to the electrons and then evolves the time-dependent Kohn-Sham equations in real space for a certain real time [33]. The dipole-strength function (or the photo-absorption cross section) is then obtained by a Fourier transform of the time-dependent dipole moment. Adiabatic LDA approximation is used in these calculations to describe exchange-correlation effects. The Octopus code uses real-space uniform grid inside the sum of spheres around each atom of the system (a single one in our case). The sphere radius and the grid spacing were taken to be 8.0 and 0.25 Å, respectively, in our calculations. The real-time propagation was performed with  $2 \cdot 10^4$  time steps with the total simulation time of about 20 fs. The Fourier transform was performed using third-order polynomial damping (see [30] for details of the code).

Shown in figure 2 are the calculated optical spectra of free  $\text{Bi}_2^-$  dimer and of interstitial  $\text{Bi}_2^-$  dimers in sixfold ring interstitial sites of networks of silica (or germania or germanosilicate), aluminosilicate, phosphosilicate and phosphogermanate glasses. Figures 3 and 4 display similar spectra for free and interstitial  $\text{Bi}^0$  atoms and for free and interstitial  $\text{Bi}^-$  ion, respectively. Comparing the

results for free  $\text{Bi}_2^-$  dimers with previous configuration interaction calculations [24, 25, 34] and those for free  $\text{Bi}^0$  with experimental and theoretical data available [35–38] (see figure 5), one readily sees that both transition wavelengths and transition intensities are described adequately in our TDDFT calculations.

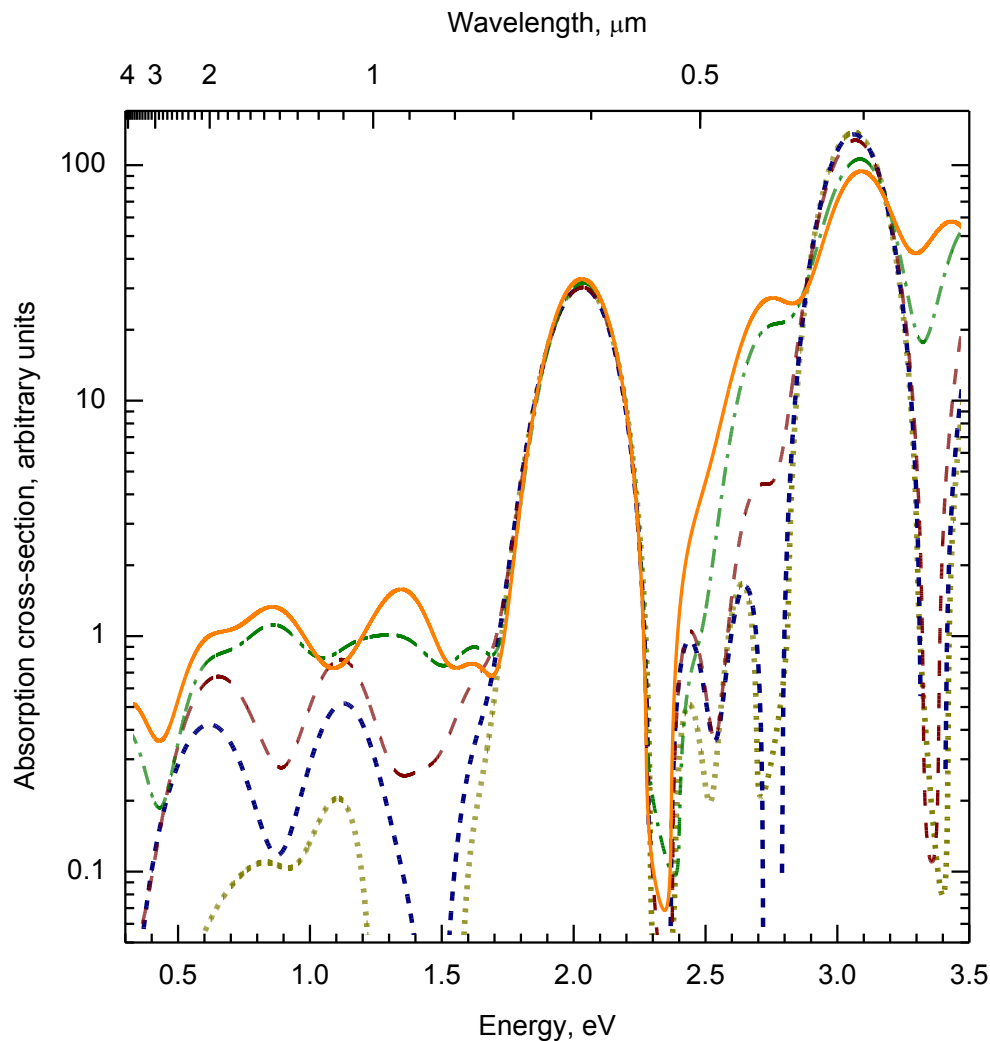


Figure 2. Optical cross-section spectra of free  $\text{Bi}_2^-$  dimer (dots) and of interstitial  $\text{Bi}_2^-$  dimers in silica, germania or germanosilicate (with low germania content) host (short dashes), aluminosilicate host (dashes), in phosphosilicate or germanosilicate (with high germania content) host (dashes plus dots) and in phosphogermanate host (solid)

Figure 2 shows calculated optical spectra of interstitial  $\text{Bi}_2^-$  dimer in comparison with those of a free dimer. Similar spectra for interstitial  $\text{Bi}^0$  atom are presented in figure 3. From figure 2 it will be noticed how optical spectrum of an interstitial  $\text{Bi}_2^-$  dimer is modified in comparison with free dimer. According to our previous calculations performed by configuration interaction

(CI) method [25], absorption at 860, 720, 460 nm and  $\lesssim 400$  nm wavelengths in the free  $\text{Bi}_2^-$  dimer is caused by transitions from the ground state to the excited ones. The IR luminescence at 1450, 1300 and 1050 nm wavelengths corresponds to spin-forbidden transitions from three lowest excited states to the ground state and the visible luminescence at 750 nm is caused to a spin-allowed transition with low oscillator strength from one of the other excited states to the ground state. Notice that comparing results of CI calculations with optical spectra calculated in TDDFT with Octopus package (such as shown in figures 2, 3, 4) one should realize that the latters include all possible transitions in the system under consideration.

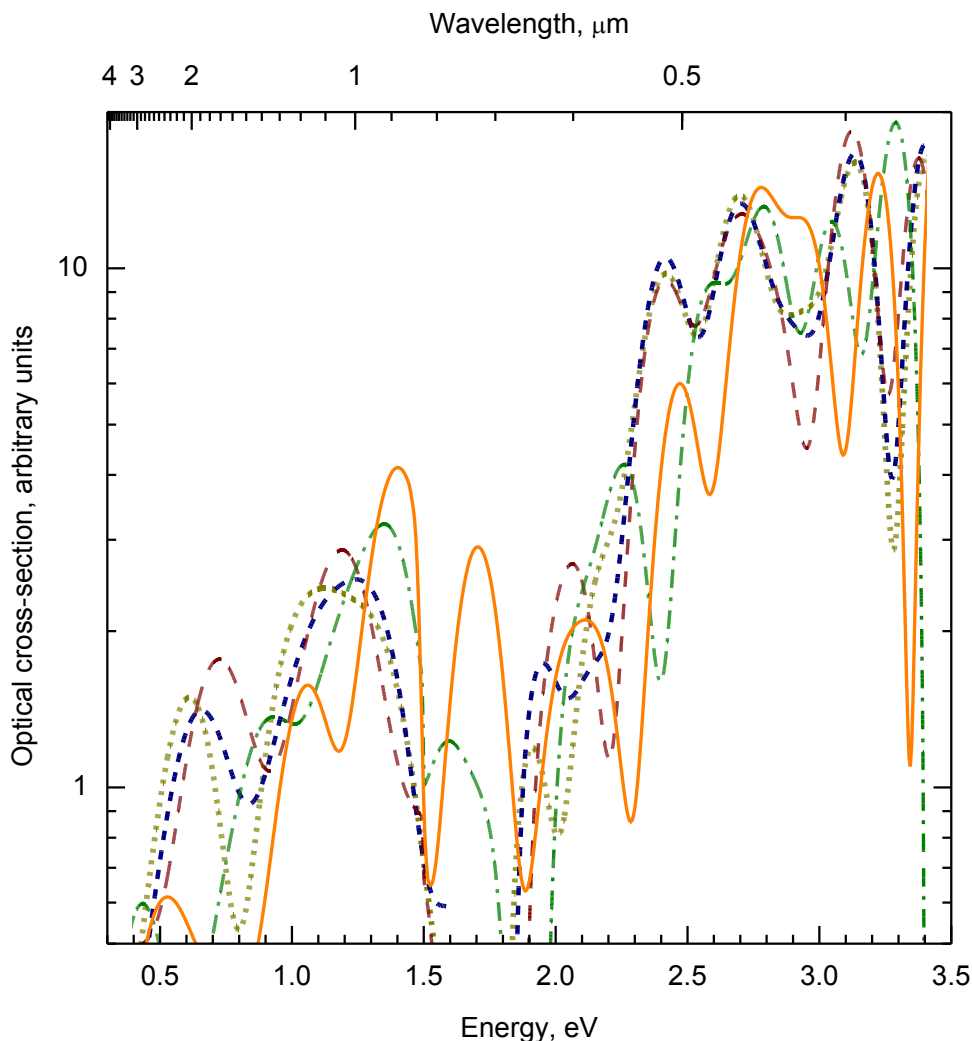


Figure 3. Optical cross-section spectra of free  $\text{Bi}^0$  atom (dots; the part for energy  $< 1.6$  eV multiplied by 10 for clarity) and of interstitial  $\text{Bi}^0$  atom in silica, germania or germanosilicate (with low germania content) host (short dashes), aluminosilicate host (dashes), in phosphosilicate or germanosilicate (with high germania content) host (dashes plus dots) and in phosphogermanate host (solid)

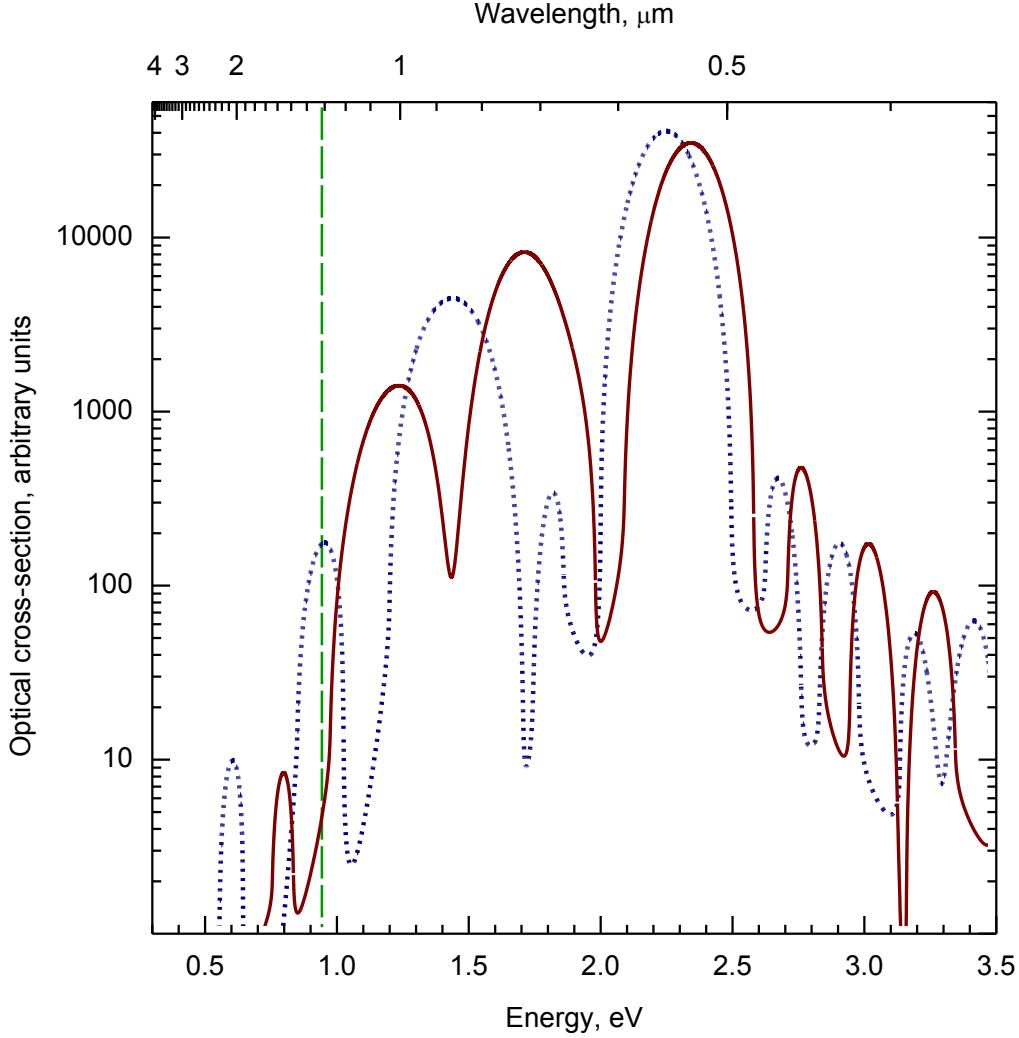


Figure 4. Optical cross-section spectra of free  $\text{Bi}^{3+}$  ion (dotted line) and of interstitial  $\text{Bi}^{3+}$  ion in aluminosilicate host (solid line).

For the interstitial  $\text{Bi}_2^{3+}$  dimers, the absorption in the  $\lesssim 400$  nm range and transitions corresponding to the absorption and visible luminescence in the 600 – 750 nm is found in our calculations to be practically unaltered in all the surrounding glass network compositions studied. The absorption band near 500 nm is found to be shifted towards shorter wavelengths (near 440 nm in phosphogermanate environment) and somewhat intensified. Besides, absorption near 800 nm grows. In phosphate-bearing and in germanosilicate (with high  $\text{GeO}_2$  content) glasses absorption in the 900 – 1000 nm range becomes significant. In glasses with no phosphate component present and in germanosilicate glasses with low  $\text{GeO}_2$  content, the IR luminescence is not too different from that in free dimers and occurring mainly in the 1000 – 1300 nm range. When passing to phosphate-bearing compositions and for high  $\text{GeO}_2$  content one finds the IR luminescence bands to be shifted towards longer wavelengths, in the 1400 – 1600 nm range.



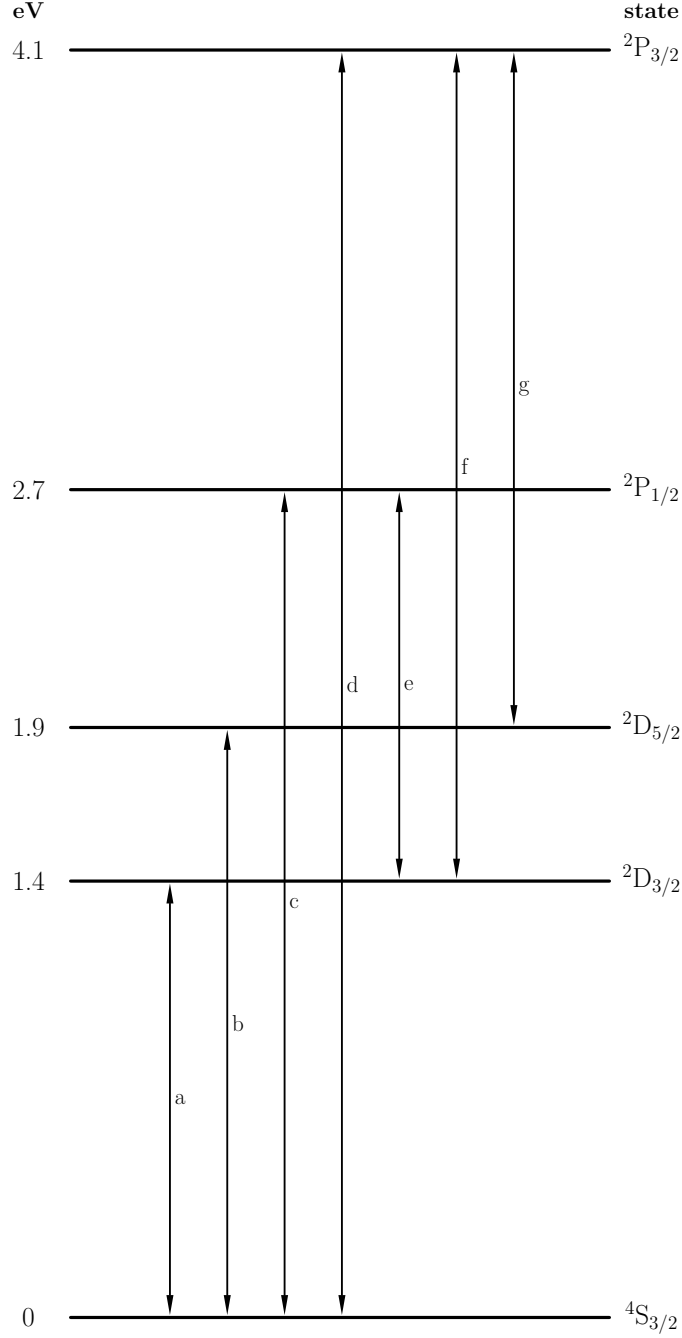


Figure 5. States, transition types and lifetimes in  $\text{Bi}^0$  atom corresponding to the  $6s^2 6p^3$  configuration [35–38]: (a) 876 nm, M1, 32 ms; (b) 648 nm, M1, 156 ms; (c) 462 nm, M1, 18 ms and E2, 161 ms; (d) 302 nm, M1, 137 ms; (e) 976 nm, M1, 833 ms and E2, 222 ms; (f) 460 nm, M1, 8 ms; (g) 564 nm, M1, 43 ms

Again, optical spectra of  $\text{Bi}^0$  interstitial atoms are found in our calculations to change compared with those of free atoms (figure 3). This change is relatively low in aluminosilicate glasses where  $\text{Bi}^0$  interstitial atoms give rise to absorption bands at  $\lesssim 400$  nm, near 500 nm and in 600 – 700 and 900 – 1100 nm ranges.

This absorption causes IR luminescence in 1000 – 1300 and 1400 – 1600 nm wavelength ranges. However the change turn out to be much more pronounced in phosphosilicate glasses and in germanosilicate glass with high germania content where the absorption should occur in 500 – 600 nm wavelength range and, especially, in 700 – 1000 nm range. The corresponding IR luminescence in these glasses is found to arise in 1000 – 1400 nm range and near 2000 nm.

The above-described modification of optical spectra of bismuth interstitial dimers and atoms with composition of surrounding glass network gives an insight into origin of variations of absorption and IR luminescence bands discovered in bismuth-doped glasses [21,23]. In particular, characteristic IR luminescence band shift from  $\sim 1100$  nm into the 1200 – 1400 nm range is observed while turning from aluminosilicate compositions to phosphate-bearing ones.

Ionization potential of the negative bismuth ion,  $\text{Bi}^-$ , is known to be rather low: e.g. in Ref. [38] the electron affinity of  $^{209}\text{Bi}$  is found to be  $7600\text{ cm}^{-1}$  or 0.94 eV. Because of this, all transitions in  $\lesssim 1300$  nm wavelength range should, in general, result in  $\text{Bi}^-$  ionization with neutral  $\text{Bi}^0$  atom formed and free electron occurred in conduction band. Since optical cross-sections in  $\text{Bi}^-$  ion are at least an order as high as those in  $\text{Bi}^0$  atom, one would expect the interstitial  $\text{Bi}^-$  ions are destroyed rapidly under both visible and IR irradiation. Thus interstitial  $\text{Bi}^-$  ions in glass may promote formation of interstitial negatively charged  $\text{Bi}_2$  dimers [25]. On the other hand, recombination luminescence in 1500 – 1700 nm range is not improbable owing to conduction electrons capturing in  $\text{Bi}^0$  interstitial atoms with  $\text{Bi}^-$  ions formed.

## Discussion

We have established, on modelling grounds, that interstitial negatively charged bismuth dimers,  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$ , can actually occur in glass network and that absorption and luminescence spectra of the dimers correlate well with the experimental spectra of bismuth-doped glasses. On the other hand, bismuth interstitial atoms,  $\text{Bi}^0$ , and negative ions,  $\text{Bi}^-$ , are demonstrated to occur in glass network as well. In particular, certain features observed in Raman spectra of bismuth-doped aluminosilicate glasses are attributable to both  $\text{Bi}_2$  dimers and Bi atoms (ions) present in glass together.

So it would appear reasonable that both  $\text{Bi}^0$  interstitial atoms and  $\text{Bi}_2^-$  ( $\text{Bi}_2^{2-}$ ) negatively charged dimers occur in bismuth-doped glasses as two types of the IR luminescence centres. Relation between interstitial  $\text{Bi}_2$  dimers and Bi atoms (and ions) concentrations in the given glass is likely to depend predominantly on bismuth dopant content. It should be stressed that in bismuth-doped glasses considerable part of the dopant bismuth atoms are likely to be bonded

with oxygen atoms of surrounding network. However such bismuth centres bear no relation to IR luminescence.

It follows from the relation between calculated intensities of transitions corresponding to absorption and IR luminescence in  $\text{Bi}^0$  atom that the IR luminescence time constant is considerably less than in  $\text{Bi}_2^-$  or  $\text{Bi}_2^{2-}$  dimers and that it decreases rapidly with electrostatic field growth (figure 3). Similar calculations of  $\text{Bi}_2$  dimers in electrostatic field prove the transition intensities to change only slightly and the transition wavelengths to change almost as rapidly as in  $\text{Bi}^0$  atom with the field strength. Therefore, interstitial  $\text{Bi}^0$  atoms should give rise to much faster IR luminescence in comparison with  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$  dimers. Unfortunately the transition intensities in atoms and dimers are hardly to be compared directly in our calculational approach. Rough estimate results in ratio of the order of 10. Thus, interstitial  $\text{Bi}^0$  atoms may be responsible for "fast" component observed in IR luminescence.

The calculations described in the present article and in Ref. [24, 25] are concerned with sixfold ring interstitial sites. The sixfold ring are known to be the most abundant ring structure in silica- and germania-based glasses network. However there are other rings as well in such glasses, mainly five-, seven- and eightfold ones. We have performed some calculations for interstitial sites formed by pairs of such rings in aluminosilicate network to examine equilibrium states of bismuth atoms and dimers and electric field strength. It is felt that the results and conclusions obtained for the sixfold rings still remain valid for sevenfold and, supposedly, in eightfold rings. The fivefold rings turn out to be too narrow to hold the interstitial dimers and, supposedly, atoms.

## Conclusion

In summary, we calculated optical spectra of interstitial negatively charged bismuth dimers,  $\text{Bi}_2^-$ , neutral atoms,  $\text{Bi}^0$ , and negative ions,  $\text{Bi}^-$ , in network of silica- and germania-based glasses with various composition. Considering our previous works [24, 25], the results of the present calculations allow definite conclusions, as follows.

- Both interstitial  $\text{Bi}_2^-$  and  $\text{Bi}_2^{2-}$  dimers and interstitial  $\text{Bi}^0$  atoms and  $\text{Bi}^-$  ions can occur in bismuth-doped silica- and germania-based glasses. IR luminescence in 1000 – 1600 nm in these glasses can be caused by all such interstitial centres.
- IR luminescence decay time in  $\text{Bi}^0$  atoms is estimated to be an order as short as in  $\text{Bi}_2^-$  or  $\text{Bi}_2^{2-}$  dimers. Hence  $\text{Bi}_2^-$  ( $\text{Bi}_2^{2-}$ ) dimers and  $\text{Bi}^0$  atoms can be assumed to cause "slow" and "fast" parts of the IR luminescence, respectively.

- Interstitial electric field strength dependence of absorption and IR luminescence in the interstitial  $\text{Bi}_2^-$  ( $\text{Bi}_2^{2-}$ ) dimers is found to differ considerably from that in the interstitial  $\text{Bi}^0$  atoms. Pronounced dependence of the IR luminescence spectra and its excitation spectra on glass composition and bismuth content observed in several experiments may be attributable to the interstitial field variations.
- interstitial  $\text{Bi}^0$  atom is found to capture under certain conditions an electron from the glass conduction band with  $\text{Bi}^-$  formed. Recombination luminescence in the 1500 – 1700 nm is likely to occur owing to such capturing. On the other hand, the interstitial negative  $\text{Bi}^-$  ions are readily destroyed under  $\lesssim 1300$  nm irradiation.

Thus our results of the present work and of Ref. [24, 25] concerning interstitial bismuth atoms and negatively charged bismuth dimers in bismuth-doped glasses provide support for the conclusion that both  $\text{Bi}^0$  and  $\text{Bi}_2^-$  ( $\text{Bi}_2^{2-}$ ) occur in these glasses as two types of the IR luminescence centres.

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